

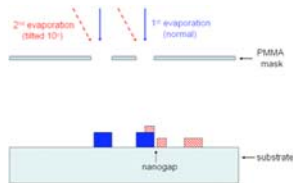
Plasmonic Nanoparticle Arrays with Nanometer Separation for High-Performance SERS Substrates

Principal Investigator: Dr. Pierre Echternach (389I)
Prof. Stephen B. Cronin, Jesse Theiss (University of Southern California)

Project Objective:

To demonstrate a new technique for fabricating arrays of plasmonic nanoparticles (NPs) with separations on the order of 1nm using an angle evaporation technique. Samples fabricated on thin SiN membranes are imaged with high resolution transmission electron microscopy (HRTEM) to resolve the small separations achieved between nanoparticles. When irradiated with laser light, these nearly touching metal nanoparticles produce extremely high electric field intensities, which result in surface enhanced Raman spectroscopy (SERS) signals. We quantify these enhancements by depositing a para-aminothiophenol (p-ATP) dye molecule on the nanoparticle arrays and spatially mapping their Raman intensity using confocal micro-Raman spectroscopy.

Method:

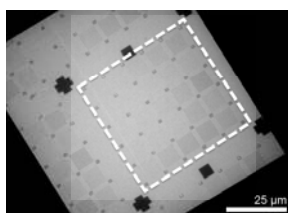


This work builds on previous research at JPL using controlled angled deposition to fabricate nano-scale tunnel junctions. A layer of ZEP-520 electron beam resist is spun on top of a layer of methyl methacrylate (MMA) resist. The more sensitive MMA layer is overexposed to produce a large undercut and a free-standing ZEP mask.

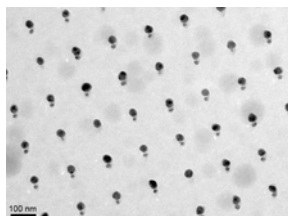
A thin layer of metal is first deposited at normal incidence. The sample is then tilted by a small angle ($5-10^\circ$), and a second layer of metal is deposited. Nano-gap size is determined by the angle of the second evaporation, θ , and the thickness of the first evaporation, t_1 . The width of the gap is given by $t_1 \cdot \tan \theta$.

Fabrication:

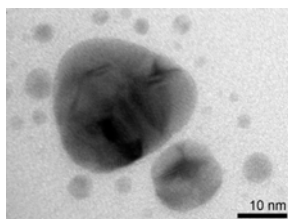
We patterned these nano-gap structures on thin SiN membranes for imaging in a JEOL JEM-2100F high resolution transmission electron microscopy (HRTEM) system. A JEOL 9300FSZ electron beam lithography system at JPL was used to write several different arrays of gold and silver nanoparticles of varying size, shape, and separation.



Low-magnification TEM image of a 5x5 matrix, each cell being a >1000 NP array.



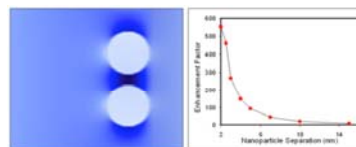
Array of NP pairs in one cell of matrix.



High-magnification TEM image of a NP pair with a gap of about 2nm, fabricated with $t_1 = 30\text{nm}$ and $\theta = 5^\circ$.

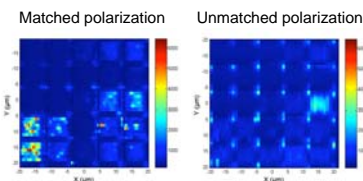
Motivation:

Optimum electric field enhancement occurs between two nearly touching metal nanoparticles (separation < 5 nm). Total Raman scattering intensity is proportional to $|E|^4$.

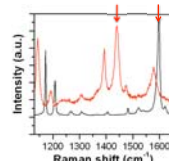


SERS Results:

Nano-gap samples were functionalized with 1mM p-ATP Raman dye solution and examined with a Renishaw inVia Raman microscope. A high accuracy motorized stage scans the sample through a 633nm laser spot focused through a 100X objective. Spatial mappings of the 5x5 cell matrix are made from the intensity of the Raman spectra at a single molecular vibrational energy.



We found that the signal intensity is significantly increased when laser polarization is aligned to match the NP pair. Estimating the molecular density within the focal volume yields enhancement factors of 10^4 for our first round of substrates.



$$E.F. = \frac{I_{SERS} / N_{ads}}{I_{bulk} / N_{bulk}}$$

Benefits to NASA and JPL (or significance of results):

The development of robust, reliable SERS substrates will enable single molecule detection and identification at low laser powers (< 1 mW) with miniature spectrometers that can be used in autonomous space applications. This work will also enable SERS to be used on flight missions by improving substrate reproducibility and shelf-life. SERS substrates will enable in situ detection and characterization of trace amounts of organic compounds present in planets, comets and asteroids.

Our results show significant enhancement when the incident laser is polarized parallel to the axis of the nanoparticle pairs while little enhancement is observed for perpendicular polarization. We estimate SERS enhancement factors of 10^4 . These results demonstrate proof-of-principle of this fabrication technique with considerable room for optimization.